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ON PERFECT SCREENING FOR CHARGED SYSTEMS.(U)
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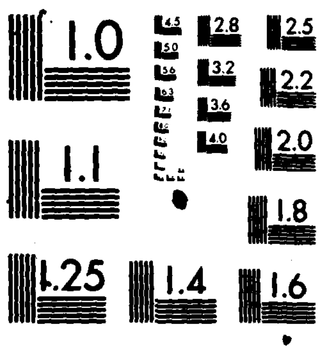

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On Perfect Screening for Charged Systems

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On Perfect Screening for Charged Systems

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Abstract

We prove that when correlations in an equilibrium classical system in ν-dimensions, $\nu \geq 2$ (> or =), containing charges decay faster than $(\text{distance})^{-(\ell+\nu)}$ then the charge cloud surrounding particles has no multipole moments of order $k \leq \ell$ (< or =). This yields $\ell+1$ sum rules with $\ell=\infty$ (infinity) when the decay is exponential. This extends previous results for $\ell \leq 2$ (< or =) sum rules and also generalizes them to systems containing fixed dipoles (or higher multipoles). Some consequences are described.

I. Introduction

We study ν-dimensional, $\nu \geq 2$, classical charged systems described by correlation functions satisfying the equilibrium BGY (stationary BBGKY) hierarchy. We proved earlier [1,2] that if the correlations have good clustering behavior then the net charge, dipole and quadropole moments of the density engendered by specifying the positions of any n-particles, must vanish. We called the resulting conditions on the $(n+1)$ th correlation function the $\ell = 0, 1, 2$ sum rules. Only the $\ell = 0$ sum rule seems to be generally known. This is the only nontrivial one for $n = 1$ in a homogenous system where it is called the electroneutrality condition. For inhomogenous systems or for $n > 1$ the $\ell = 1, 2$ sum rules are also relevant and useful [3,4].

The origin of the sum rules lies in the long range nature of the Coulomb forces. They are unaffected by any finite range interactions, e.g. hard cores, between the particles. They express the fact that correlations cannot decay "faster" than the total, i.e. direct plus induced, interactions. Indeed the

arguments show that systems with power law potentials, e.g. Lenard-Jones, have similar power law decay of the correlations [1]. What is remarkable about Coulomb systems, i.e. real matter, is that correlations can and often do decay much faster than any power law. Exponential or faster decay can be proven rigorously in one dimension, for a one component plasma in $\nu = 2$ at $\beta e^2 = 2$ [4] and at high temperatures and low densities in all dimensions [5]. Exponential decay of correlations is in fact expected to hold generally in the fluid phase of charged systems—an expectation based on experiment, computer simulation and approximate theories [6].

In this note we extend our previous results for $\ell \leq 2$ to arbitrary ℓ: whenever the correlations decay faster than $r^{-(\ell+\nu)}$ then the charge density in the vicinity of any particles contains no multipoles of order less or equal to ℓ. In particular, exponential decay implies an infinite number of such sum rules. Another extension of our results is the inclusion of particles with permanent dipoles (or higher multipoles) in the charged system (pure dipoles are known not to screen).

II. Results

We consider a mixture of charged particles and permanent dipoles moving in the whole ν-dimensional space R^ν or in a restricted domain $\mathcal{D}$ defined by appropriate walls. The particles of species α carry a charge e_α and a permanent dipole moment of strength d_α ; for some α, d_α or/and e_α can be zero. We denote by r and ω respectively the position of the particle

and the orientation of its dipole moment $\mu = d_\alpha \omega$, and use the notation $q = (\alpha, r, \omega)$ and

$$\int dq = \int_{\mathcal{D}} d\underline{r} \int d\underline{\omega} \sum_{\alpha} \, , \qquad \int d\underline{\omega} \cdot 1 = 1$$

The particles are subject to the action of external forces and interact by two-body forces of the form

$$F(q_1; q_2) = F_\Lambda(q_1; q_2) + F_L(q_1; q_2) = F_{\alpha_1, \alpha_2}(r_1 - r_2; \omega_1, \omega_2) \quad (1)$$

The finite range part F_Λ includes in particular strong local repulsion or hard core and F_L consists of charge-charge, charge-dipole and dipole-dipole terms. The external forces can include a fixed charge density in $\mathcal{D}$, e.g. jellium [2]. We assume that the dielectric constant ϵ is the same inside and outside $\mathcal{D}$ and set $\epsilon = 1$. The case of different dielectric media will be treated elsewhere, c.f. [4].

We denote by $\rho(q_1)$, $\rho(q_1 q_2)$, ... the singlet densities, the pair correlation functions, etc.... and introduce the truncated (Ursell) functions

$$\rho^T(q_1 q_2) = \rho(q_1 q_2) - \rho(q_1)\rho(q_2) \quad (2)$$

$$\rho^T(q_1 q_2 q_3) = \rho(q_1 q_2 q_3) - \rho(q_1)\rho(q_2 q_3) - \rho(q_2)\rho(q_1 q_3) - \rho(q_3)\rho(q_1 q_2) + 2\rho(q_1)\rho(q_2)\rho(q_3), \ldots \quad (3)$$

As usual the equilibrium ρ at temperature T are assumed to satisfy the stationary BBGKY-equations [2]

$$k_B T \nabla_1 \rho(q_1) = F(q_1) + \int dq\, F(q_1;q)\,\rho^T(q_1\, q) \tag{4a}$$

$$k_B T \nabla_1 \rho(q_1 q_2) = [F(q_1) + F(q_1, q_2)]\, \rho(q_1 q_2) + \int dq\, F(q_1;q)[\rho(q_1 q_2 q) - \rho(q)\rho(q_1 q_2)], \ldots \tag{4b}$$

where $F(q_1)$ represents the total <u>average force</u> on particle 1.

We shall always assume that the truncated correlation functions are absolutely integrable,

$$\int dq_1 \,|\rho^T(q_1 \cdots q_n)| < \text{Const.} \quad , \; n \geq 2 \tag{5}$$

<u>Moment Relations</u>

Let $\rho(q\,|\,q_1 \cdots q_m)$ be the <u>excess particle density</u> of species α <u>given</u> that there are particles of species $\alpha_1, \cdots, \alpha_m$ at $r_1, \cdots, r_m$,

$$\rho(q\,|\,q_1 \cdots q_m) = [\rho(q\; q_1 \cdots q_m)/\rho(q_1 \cdots q_m) - \rho(q)] + \sum_{i=1}^{m} \delta(q;q_i) \tag{6}$$

where $\delta(q;q_i) = \delta_{\alpha,\alpha_i}\,\delta(r - r_i)\,\delta(\omega - \omega_i)$. The (l,m) moment relation expresses the fact that $M(l;m)$ the multipole moment tensor of order l due to $\rho(q\,|\,q_1 \cdots q_m)$ vanishes.

$$M(l;m) = \int dq\, T_l(q)\, \rho(q\,|\,q_1 \cdots q_m), \tag{7}$$

$T_0(q) = e_\alpha$, $T_1^a(q) = e_\alpha r^a + d_\alpha \omega^a$, $T_2^{ab}(q) = e_\alpha r^a r^b + \frac{1}{2} d_\alpha(\omega^a r^b + \omega^b r^a) - \frac{1}{\nu}(e_\alpha |r|^2 + d_\alpha\, \omega\cdot r)\,\delta^{a,b}$, $a,b = 1, \cdots \nu$.

We also write out more explicitely the $M(\ell;2) = 0$ for the three dimensional homogeneous one component plasma (OCP)

$$\rho \int d^3 r \; |r|^{\ell} P_{\ell}(\theta) \left[g_3(\underline{r}, \underline{r}_1) - g(r) \right] = -\left(\frac{4\pi}{2\ell+1}\right) |r_1|^{\ell} \rho(r_1) \tag{8}$$

Where $P_{\ell}(\theta)$ is the $\ell^{\underline{th}}$ order Legendre polynomial, θ is the angle between $\underline{r}$ and $\underline{r_1}$, and $\underline{r_2} = \underline{0}$.

We now state our main results.

<u>Theorem</u>: Let $\mathcal{D} \subseteq R^{\nu}$, $\nu \geq 2$, contain an open ν-dimensional cone in which the asymptotic densities of charged particles do not all vanish. If the correlations satisfy the condition

$$\left| r^{\ell+\nu+\varepsilon} \rho^{T}(q_1 \cdots q_k) \right| < \text{Const.} \tag{9}$$

for some $\epsilon > 0$, $r = |r_i - r_j|$, $i, j = (1, \cdots, k)$, $k = 2, \ldots, n+1$ then all the moments $M(\ell'; n')$, $\ell' \leq \ell$, $n' \leq n$ vanish.

We sketch the proof of $M(\ell; 1) = 0$ for a system of pure charges in $\nu = 3$. The general case is similar.

<u>Proof</u>: Combining (3) and (4) gives

$$\rho(q_1)\rho(q_2) \int F(q : q_1)\, \rho(q | q_2)\, dq = k_B T\, \nabla_1 \rho^{T}(q_1 q_2)$$
$$- \left[F(q_1) + F(q : q_2) \right] \rho^{T}(q_1 q_2) - \int F(q ; q_1)\, \rho^{T}(q\, q_1 q_2)\, dq$$

Let $\hat{r}_1 = r_1/|r_1|$ be a fixed unit vector in the open cone contained in $\mathfrak{S}$. Lemma 1 and 2 of [2] show, using (9), that the right hand side of (10) decays faster than $|r_1|^{-(\nu+\ell-1)}$ as $|r_1| \to \infty$. This yields $M(0;1)=0$

Proceeding by induction, let us assume that

$$M_m(k;1) = \int dq\, e_1 |r|^k\, Y_{km}(\hat{r})\, \rho(q|q_2) = 0, \quad k = 1, \dots, \ell-1, \quad |m| \le k$$

where $Y_{k,m}$ are the spherical harmonics.

The multipole expansion of the Coulomb potential gives the identity

$$\frac{(-1)^k}{k!}\, \partial_{a_1 \cdots a_k}\left(\frac{\hat{r}_1}{|r_1|^{\nu-1}}\right) \int dq\, e_1\, r^{a_1} \cdots r^{a_k}\, \rho(q|q_2)$$
$$= (4\pi/2k+1) \sum_{m=-k}^{k} \nabla_1 \left(Y^*_{1m}(\hat{r}_1)/|r_1|^{k+1} \right) M_m(k;1) \tag{11}$$

One can therefore subtract in the integrand on the left hand side of (10) the $\ell-1$ first terms of the Taylor expansion of the

force $F(q;q_1)$ about r_1. Lemma 1 of [2] implies then

$$\partial_{a_1 \cdots a_\ell} \left(\frac{\hat{r}_1}{|r_1|^{\nu-1}} \right) \Big|_{|r_1|=1} \int dq \, e_2 \, r^{a_1} \cdots r^{a_\ell} \, \rho(q/q_2) = 0$$

Taking the scalar product of the above equation with $\hat{r}_1$ and using (11) yields

$$\sum_{m=-\ell}^{\ell} Y^{*}_{\ell m}(\hat{r}_1) \, M_m(\ell;1) = 0 \tag{12}$$

for an open jet of unit vectors $\hat{r}_1$, and hence $M(\ell;1)=0$.

III. Discussion

As already mentioned in the introduction there is a wide range of physical conditions in which systems containing free charges are expected and in some cases are proven to cluster exponentially fast. In these circumstances the shielding of fixed charges is perfect—the excess particle density carries no multipole moments of any order. This was indeed verified explicitely by Jancovici [4] for the $\nu=2$ OCP at $\beta e^2=2$.

It would seem useful and it may even be important to take this fact into account when constructing approximate theories

of plasmas, ionic salts, molten metals, etc. If one already has a pair correlation function, obtained from some approximate theory, e.g. HNC, MSA, and wants to obtain information about the higher order correlations, as would be necessary for obtaining micro-field distributions in a plasma, then one should only use constructions which respect the sum rules. Similar caution needs to be used in deriving approximate integral equations for the pair correlation by making some clousure ansatz in the BGY hierarchy. In this connection it is is interesting to observe that the Totsuji-Ichimura convolution approximation [7] usually considered for the homogenous OCP but readily extended to the general case

$$\rho^T(q_1\, q_2\, q_3) = \rho^T(q_1\, q_2)\rho^T(q_2\, q_3)/\rho(q_2) + \rho^T(q_2 q_3)\rho^T(q_3 q_2)/\rho(q_3) + \rho^T(q_3\, q_1)\rho^T(q_1\, q_2)/\rho(q_1) + \int dq_4\, \rho^T(q_1 q_4)\rho^T(q_2 q_4)\rho^T(q_3 q_4)/\rho^2(q_4) \tag{13}$$

does indeed satisfy $M(\ell;2) = 0$ whenever $M(\ell;1) = 0$.

This is perhaps not surprising since (13) is correct to first order in the plasma coupling parameter but may be responsible for the good results one obtains with this approximation [7] and should be preserved in modifications designed to improve its short distance behavior.

Systems with Walls

It appears, rather surprisingly, that when $\mathcal{D}$ is equal to the half-space, i.e. $r^{\perp} > 0$, then correlations "parallel to the wall" decay like $r_{11}^{-\nu}$. This can be verified explicitely for the OCP in $\nu = 2$ at $\beta e^2 = 2$ and perturbationally in the general case [4]. An extension of our theorem shows that this is sufficient for the $\ell = 0$ sum rule but not for $\ell > 0$ [8]. Indeed we argue [3,8] that stronger decay which would imply the $\ell = 1$ sum rule would have some very unphysical consequences.

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